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Research Article

Regiochemistry and mechanism of oxidation of *N*-benzyl-*N*-alkylhydroxylamines to nitrones

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Abstract

The oxidation of various *N*-(*o*-, *m*-, *p*-substituted benzyl)-*N*-alkylhydroxylamines and their dideuteriobenzyl ($PhCD_2$) counterparts was carried out using mercury(II) oxide and *p*-benzoquinone (*p*-BQ) as oxidants. An overwhelming preference for the formation of conjugated nitrones is observed in the oxidation of *N*-benzyl-*N*-isopropylhydroxylamines. Considerable intra- and intermolecular kinetic isotope effects and negative ρ values in the Hammet plots point towards a mechanistic pathway that involves electron transfer from nitrogen to the oxidant followed by hydrogen abstraction. The conformation of unstable (*E*)-nitrones, which readily isomerize to the more stable (*Z*)-nitrones, is deduced from ^1H NMR data. The $E \rightleftharpoons Z$ isomerization was found to be a bimolecular process.

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